

SYSTEM AND METHOD FOR SELECTIVE ETCHING OF SILICON NITRIDE DURING SUBSTRATE PROCESSING

Cross-Reference to Related Application

[0001] The present application claims the benefit of United States Provisional Application Number 60/533,097, filed December 30, 2003, the entirety of which is incorporated herein by reference.

Background of the Invention

[0002] As the dimensions of the microelectronic devices continuously decrease in size, now into the low nm scale, the wafer surface preparation procedures play an increasingly important role in IC manufacturing. The process chemicals, sequence, and number of cleaning steps are becoming more critical in determining the desired end results. As semiconductor manufacturing continues to advance, smaller and smaller devices are being designed and built on the same wafer surface area. These fine structures have created a new set of processing issues to the fab engineers and scientists. One of these problems is selectively etching silicon nitride (Si_3N_4) as compared to underlying silicon oxide films.

[0003] The etching of Si_3N_4 is currently achieved in a variety of ways, including plasma dry etching or reactive ion etching (RIE). However, RIE of Si_3N_4 fails to offer high selectivity to the underlying oxide films. In addition, RIE of Si_3N_4 can degrade, in the form of surface pitting, the underlying film or the silicon substrate. Another existing way to etch Si_3N_4 is through the application of phosphoric acid (H_3PO_4). The use of H_3PO_4 has been historically used due to its high etch selectivity of Si_3N_4 as compared to silicon dioxide (SiO_2). A typical Si_3N_4 etching reaction using H_3PO_4 can be described as follows:



[0004] In this reaction, water hydrolyzes Si_3N_4 to form hydrous silica and ammonia. The ammonia remains in solution to form ammonium phosphate. The reaction suggests that water is an integral part of the chemistry to etch Si_3N_4 . As nitride is etched, hydrated SiO_2 (H_2OSiO_2) is formed in the solution and inhibits the etching of SiO_2 , i.e. it results in a higher selectivity. The SiO_2 etching continues to decrease, as shown in FIGS. 1 and 2, until the

system (phosphoric acid liquid and wafers) reaches equilibrium (no mass transport), which at that time it stops. Once equilibrium is reached, an SiO_2 film apparently re-deposits. The bath life will be determined depending on the tolerance that a fab can allow with this re-deposition. While this slow of oxide etch rate is beneficial (i.e. higher selectivity) but this re-deposition will cause high particle counts on the wafer which is undesirable. This phenomenon is so noticeable that it can be predicted. As shown in Fig. 2, the particle levels were in about 40 particles added up to 21 x50 wafer processed in the bath after which a considerable increase in these counts was noticed.

[0005] While a number of processes have been developed in an attempt to more selectively etch Si_3N_4 in comparison to silicon oxides during semiconductor manufacturing, existing systems are less than optimal and suffer from a number of drawbacks. For example, in United States Patent 6,376,261 (the '261 Patent), a system is disclosed that has a control scheme to predict the etch rate at the wafer surfaces. This system measures the thickness of a thin film on the wafers and adjusts the system parameters based on the film thickness measurements of the previous run. The adjustments are done in between wafer batches, resulting in manufacturing down time and decreased etching selectivity within each batch of wafers as the etching solution becomes contaminated and/or the concentration ratio of its components change over time. Additionally, the system disclosed in the '261 Patent requires an advanced process control system (APC) at the IC fab level.

[0006] Additional etching systems are disclosed in United States Patent 3,715,249 (the '249 Patent), United States Patent 6,087,273 (the '273 Patent), and United States Patent 5,885,903 (the '903 Patent). While these systems attempt to achieve selective etching, using a mix of sulfuric and phosphoric acid, these systems do not contain a control system to ensure maximum selectivity in the etching by controlling process and mixture parameters. Thus, these systems result in decreased etching selectivity within each batch of wafers as the etching solution becomes contaminated and/or the concentration ratio of its components change over time.

[0007] In United States patent 5,310,457, an etching system is disclosed that utilizes the addition of HF and nitric acids to phosphoric acids to increase the etching selectivity of nitride to silicon oxide. However, the addition of HF and nitric acids to phosphoric acids has proved to be less than optimal in performance.

[0008] Finally, while some prior art etching systems and methods can achieve high selectivity in etching silicon nitride to silicon dioxide, maximization of etch selectivity is not a satisfactory sole goal. Consistent and steady etch rates for both the silicon nitride etch and the silicon oxide etch are also desirable. As mentioned above, FIG. 1 shows the results obtained from a conventional silicon nitride etch system using phosphoric acid (85% wt) at 165 C. As you can be seen, the nitride etch rate is stable while the oxide etch rate decreases with the number of wafers processed. Similar behavior is shown in FIG. 2 where the nitride and oxide etch rates were monitored against time in hours. The selectivity (i.e., the silicon nitride etch rate/silicon oxide etch rate) is plotted in FIG. 3. Because of the continuous drop in silicon oxide etch rate, the selectivity is obviously increasing with time. While this trend is a good one because it provides minimized silicon oxide loss, it also restricts the type of wafers that can be processed. Typically, wafers are soaked in the etching acid for a period of time. Thus, while the silicon nitride etch rate is fixed, the amount of silicon oxide removed will vary from lot to lot and hence the device dimensions will vary, resulting in varied performance. For obvious reasons, this is undesirable. Additionally, with continuous processing of wafers in this fashion, particles (from the etch by-products) will build up in the bath and eventually depositing on the wafers, as depicted in FIG. 4. The on-wafers particles remain at an acceptable level (<40 @0.16 um) for up to 20x50x200 mm wafers processed in the bath (1500 A were removed from each wafers). At that point, the bath needs to be drained and filled again with fresh acid to start a new processing cycle. In this scenario, it takes about 2 hours to drain/fill/heat the bath, which minimizes the utilization of the bath. Thus, the variability of etch rate is the main drawback for existing silicon nitride etch systems and methods.

Summary of the Invention

[0009] It is therefore an object of the present invention to provide a system and method for etching silicon nitride from at least one substrate that results in increased etching selectivity of silicon nitride to silicon oxides.

[0010] Another object of the present invention to provide a system and method for selectively etching silicon nitride from at least one substrate that provides dynamic control of processing conditions and parameters.

[0011] Yet another object of the present invention to provide a system and method for etching silicon nitride from at least one substrate that provides dynamic control of processing conditions and parameters based on component concentration ratios and/or silicate concentration of the etching mixture.

[0012] Still another object of the present invention to provide a system and method for etching silicon nitride from at least one substrate that does not require an APC system (APC) at the IC fab level, but rather at the nitride etch tool level.

[0013] A further object of the present invention to provide a system and method for etching silicon nitride from at least one substrate that allows real time measurements of particle contaminants in a phosphoric (or phosphoric/sulfuric) bath.

[0014] A still further object of the present invention to provide a system and method for etching silicon nitride from at least one substrate that provides a stable silicon nitride etch rate, reduces variations in oxide etch rate, and/or reduces particle contaminations build up in the etchant.

[0015] A yet further object of the present invention to provide a system and method for etching silicon nitride from at least one substrate that affords high and stable selectivity of the etching over the entire bath life, stable silicon nitride and silicon oxide etch rates, minimum oxide loss, longer bath life (and hence lower cost of ownership), acceptable particle levels on the substrates, and/or a reduction in the number of processing steps.

[0016] These and other objects are met by the present invention, which in one aspect, is a method of etching silicon nitride from at least one substrate comprising: providing a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber; supplying sulfuric acid, phosphoric acid, and water to the closed-loop circulation system in predetermined amounts so as to form a mixture having a predetermined concentration ratio and a predetermined volume, the mixture filling the process chamber and overflowing into the recirculation line; submerging at least one substrate in the mixture within the process chamber; circulating the mixture through the closed-loop circulation system; continuously measuring concentration ratio of the mixture with a concentration sensor; comparing the measured concentration ratio to the predetermined concentration value to determine whether the measured concentration value is within a predetermined range of the predetermined concentration ratio; and upon determining that the measured concentration

ratio is not within the predetermined range of the predetermined concentration ratio, automatically feeding a volume of sulfuric acid, phosphoric acid, and/or water into the closed-loop circulation system while bleeding a substantially equal volume of the mixture from the closed-loop circulation system that will return the concentration ratio of the mixture back within the predetermined range during processing of the at least one substrate.

[0017] In one embodiment, this aspect of the inventive method can further comprise: continuously measuring particle counts in the mixture with a particle counter; comparing the measured particle count to a predetermined particle count to determine whether the measured particle count is greater than the predetermined particle count; and upon detecting the mixture having a particle count that is greater than the predetermined particle count, automatically bleeding a volume of the mixture from the closed-loop circulation system and feeding a substantially equal volume of sulfuric acid, phosphoric acid, and/or water into the closed-loop circulation system that will return the particle count of the mixture back to or below the predetermined particle count during processing of the at least one substrate.

[0018] In another aspect, the invention is a method of etching silicon nitride from at least one substrate comprising: (a) supplying sulfuric acid, phosphoric acid, and water to a process chamber in predetermined amounts so as to form a predetermined volume of mixture having a predetermined concentration ratio; (b) circulating the mixture through the process chamber in a closed-loop circulation system; (c) submerging at least one substrate in the mixture within the process chamber; (d) bleeding a volume of mixture from the closed loop system so as to reduce the effect of etch-by-products in the circulating mixture; and (e) feeding phosphoric acid, sulfuric acid, and/or water to replace the volume of mixture bled from the closed loop; wherein the volume bled is selected to maintain or return the concentration ratio of the mixture to within a predetermined range of the predetermined concentration ratio.

[0019] In this aspect, the invention in some embodiments can be performed so that the bleeding and feeding of steps (d) and (e) is performed continuously or at set intervals. In other embodiments, this aspect of the invention can also comprise the steps of: (f) continuously measuring the concentration ratio of the mixture with a concentration sensor during processing of the at least one substrate; (g) comparing the measured concentration ratio to the predetermined concentration value to determine whether the measured concentration value is within a predetermined range of the predetermined concentration ratio; and (h) upon

determining that the measured concentration ratio is not within the predetermined range of the predetermined concentration ratio, automatically performing steps (d) and (e).

[0020] In yet another aspect, the invention is a system for etching silicon nitride from at least one substrate comprising: a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber; means for supplying sulfuric acid, phosphoric acid, and water to the closed-loop circulation system so as to form a predetermined volume of mixture having a predetermined concentration ratio; means for flowing the mixture through the closed-loop circulation system; a concentration sensor that continuously measures the concentration ratio of the mixture and produces a signal indicative of the measured concentration ratio during processing of at least one substrate in the process chamber; means for feeding sulfuric acid, phosphoric acid, and water to the closed-loop circulation system; means for bleeding the mixture from the closed-loop circulation system; and a processor operably coupled to the concentration sensor, the feeding means, and the bleeding means; wherein the processor is programmed so that upon receiving a signal indicative of a concentration ratio that is not within a predetermined range of the predetermined concentration ratio from the concentration sensor, the processor automatically activates the feeding means to add a volume of sulfuric acid, phosphoric acid, and/or water to the closed-loop circulation system and activates the bleeding means to drain a substantially equal volume of the mixture from the closed-loop circulation system during the processing of the at least one substrate that will return the concentration ratio of the mixture within the predetermined range of the predetermined concentration ratio.

[0021] In some embodiments, the inventive system may further comprise: a particle counter that continuously measures particle count of the mixture and produces a signal indicative of the measured particle count during processing of at least one substrate in the process chamber; wherein the processor is also operably coupled to the particle counter; and wherein the processor is further programmed so that upon receiving a signal indicative of a measured particle count above a predetermined particle count, the processor automatically activates the feeding means to add a volume of sulfuric acid, phosphoric acid, and/or water to the closed-loop circulation system and activates the bleeding means to drain a substantially equal volume of the mixture from the closed-loop circulation system during the processing of the at

least one substrate that will return the particle count of the mixture back to or below the predetermined particle count.

[0022] In a still further aspect, the invention is a method of etching silicon nitride from at least one substrate comprising: providing a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber; supplying a predetermined volume of an etchant to the closed-loop circulation system, the etchant filling the process chamber and overflowing into the recirculation line; submerging at least one substrate in the etchant within the process chamber; circulating the mixture through the closed-loop circulation system; continuously measuring particle count of the etchant with a particle counter; upon detecting the etchant having a measured particle count above a predetermined particle count, automatically bleeding a volume of contaminated etchant from the closed-loop circulation system while replacing the volume by feeding fresh etchant into the closed-loop circulation system during the processing of the at least one substrate that will return the particle count of the etchant within the closed-loop circulation system to or below the predetermined particle count.

Brief Description of the Drawings

[0023] Figure 1 is a graph comparing nitride and oxide etch rates as a function of the number of wafers processed using a prior art phosphoric acid only mix.

[0024] Figure 2 is a graph comparing nitride to oxide etch rates as a function of time for batches of fifty 200 mm wafers using a prior art phosphoric acid only mix.

[0025] Figure 3 is a graph illustrating the selectivity of the silicon nitride etch rate to the silicon oxide etch rate as a function of time for batches of fifty 200 mm wafers using a prior art phosphoric acid only mix.

[0026] Figure 4 is a graph comparing particles and etch rate as a function of the number of processed wafers using a prior art phosphoric acid only mix.

[0027] Figure 5 is a schematic illustration of a selective etching system according to one embodiment of the present invention.

[0028] Figure 6 is a high level flow chart followed by the system controller in operating the selective etching system of FIG. 5 according to one embodiment of the present invention.

[0029] Figure 7 is graph depicting a typical operation and control scheme of the nitride etch system of FIG. 5 measuring particle contamination levels according to one embodiment of the present invention.

[0030] Figure 8 is a graph illustrating stability of silicon nitride and silicon oxide etch rates using the feed and bleed algorithm for a phosphoric acid only etchant according to an embodiment of the present invention.

[0031] Figure 9 is a graph illustrating stability of silicon nitride and silicon oxide etch rates using the feed and bleed algorithm for a phosphoric acid-sulfuric acid mixture etchant according to an embodiment of the present invention.

[0032] Figure 10 is a graph illustrating the stability of particle contamination of wafers when processed according to an embodiment of the present invention.

Detailed Description of the Drawings

[0033] FIG. 1 is a schematic representation of a substrate etching system **100** according to an embodiment of the present invention. The substrate etching system **100** comprises a process chamber **10**, a sulfuric acid (H_2SO_4) dispense line **20**, a phosphoric acid (H_3PO_4) dispense line **21**, a water (H_2O) dispense line **22**, an H_2SO_4 feed line **30**, an H_3PO_4 feed line **31**, an H_2O feed line **32**, a recirculation line **40**, a process controller **200**, a concentration sensor **50**, a particle counter **55**, a pump **60**, a heater **70**, a filter **80**, and a bleed line **90**. Adjustable valves **23-25** are operably coupled to the dispense lines **20-22** respectively to control the flow of the respective fluids therethrough. Similarly, the adjustable valves **33-35** are operably coupled to the dispense lines **30-32** respectively to control the flow of the respective fluids therethrough.

[0034] While not illustrated, the H_2SO_4 dispense line **20** and the H_2SO_4 feed line **30** are each operably coupled to a source of H_2SO_4 , such as an auxiliary drum or reservoir. The H_2SO_4 dispense line **20** and the H_2SO_4 feed line **30** can be coupled to the same or different sources of H_2SO_4 , depending on processing needs and/or space restrictions. Similarly, the H_3PO_4 dispense line **21** and the H_3PO_4 feed line **31** are each operably coupled to a source of H_3PO_4 . The H_3PO_4 dispense line **21** and the H_3PO_4 feed line **31** can be coupled to the same or different sources of H_3PO_4 , depending on processing needs and/or space restrictions. The H_2O dispense line **22** and the H_2O feed line **32** are each operably coupled to a source of H_2O .

H₂O dispense line **22** and the H₂O feed line **32** can be coupled to the same or different sources of H₂SO₄, depending on processing needs and/or space restrictions.

[0035] The process chamber **10** comprises a recirculation weir **11** and a processing volume **12**.

A pair of inlet manifolds **13** are provided at the bottom of the processing volume **12** of the process chamber **10** for introducing fluids into the processing volume **12**. the processing volume **12** is of sufficient size such that plurality of wafers **14** can be supported therein.

While the wafers **14** are illustrated as being supported in a vertical orientation, the wafers can also be oriented in a horizontal orientation. Additionally, the process chamber **10** can be designed for single-wafer processing.

[0036] The process chamber **10** also comprises a bleed line **90**. The bleed line **90** is fluidly coupled to a bleed port (not illustrated) of the process chamber **10** so that liquids can be drained from the process volume **12** of the process chamber **10** during wafer processing. An adjustable bleed valve **91** is operably coupled to the bleed line **90** so that the flow rate (mass or volumetric) of fluids through the bleed line **90**, and thus out of the closed-loop circulation system, can be controlled.

[0037] One end of the recirculation line **40** is fluidly coupled to a hole in the bottom of the recirculation weir **11** so that any liquid that overflows the processing volume **12** into the recirculation weir **11** can be drawn into the recirculation line **40** if desired. The other end of the recirculation line **40** is fluidly coupled to the inlet manifolds **13**. The recirculation line **40** forms a fluid pathway from the recirculation weir **11** to the processing volume **12** of the process chamber **10**. Thus, the recirculation line **40**, combined with the process chamber **10**, forms a closed-loop circulation system.

[0038] The pump **60**, the heater **70**, and the filter **80** are all operably and fluidly coupled to the recirculation line **40**. As such, liquid that passes through the recirculation line **40**, can be heated to a desired temperature by the heater **70**. The filter **80** can remove ionic and/or particulate contaminants from the liquid as it passes through the recirculation line **40**. The concentration sensor **50** and the particle counter **55** are also operably coupled to the recirculation line **40** so that they can take the appropriate measurements of any fluid passing through the recirculation line **40**. The concentration sensor **50** can be any instrument capable of analyzing a mixture to determine the concentration ratio of its component parts, such as an NIR spectrometer or an FT-NIR spectrometer. The particle counter **55** can be any instrument

capable of counting particles in a liquid, such as for example a liquid borne particle counter, which are standard in the art.

[0039] The process controller **200** is operably connected to the adjustable valves **33-35**, the concentration sensor **50**, the particle counter **55**, and the bleed valve **91** for communication therewith. These operable connections can be facilitated via the appropriate electric, fiber-optic, cable, or other suitable connections. In FIG. 5, the operable connections of the component **33-35**, **50**, **55**, **91** with the process controller **200** are illustrated as dotted lines. The process controller **200** is a suitable microprocessor based programmable logic controller, personal computer, or the like for process control and preferably includes various input/output ports used to provide connections to the various components **33-35**, **50**, **55**, **91** of the etching system **100** that need to be controlled and/or communicated with.

[0040] The process controller **200** also preferably comprises sufficient memory to store process recipes, parameters, and other data, such as a predetermined (i.e. target) concentration ratio, a predetermined particle count, a predetermined range, flow rates, processing times, processing conditions, and the like. The process controller **200** can communicate with any and all of the various components of the etching system **100** to which it is operably connected in order to automatically adjust process conditions, such as activating flow through any one of feed lines **30-32** either alone or in combination, activating flow through bleed line **90**, pump activation, heat application, and filtering. While not illustrated, the process controller **200** can also be operably coupled to the heater **70**, the pump **60**, the inlet manifolds **13**, and the adjustable valves **23-25** if desired.

[0041] The process controller **200** is also programmed with the proper algorithms to receive data signals from the concentration sensor **55** and the particle counter **55**, analyze the incoming data signals, compare the values represented by the incoming data signals to stored values and ranges, and automatically make the appropriate adjustments to the etchant being used to process the wafers **14** by feeding fresh etchant components into the circulation via lines **30-32** and/or bleeding contaminated/old etchant via bleed line **90** to achieve a predetermined characteristic within the etchant mixture. For example, the process controller **200** can store a predetermined value and a predetermined acceptable operating range for concentration ratio or particle count. This will be discussed in more detail below with respect to operation of the

system **100**. The type of process controller used depends on the exact needs of the system in which it is incorporated.

[0042] Operation of an etching system according to an embodiment of the present invention will be discussed. For ease of discussion, the method will be discussed in relation to the etching system **100** of FIG. 5 with the understating that other variations, modifications, and etching systems can be used to perform the etching process.

[0043] A plurality of wafers **14** in need of etching are provided. The wafers **14** preferably are silicon wafers for IC manufacturing and comprise layers of both silicon nitride (Si_3N_4) and silicon oxide (SiO_2) thereon. However, other types of substrates can be used, such as MEMS substrates, flat panel displays, etc. All valves **23-25**, **33-35**, **90** are in a closed position at the beginning of the process.

[0044] First, the adjustable valves **23-25** are switched to an open position so that liquid H_2SO_4 , H_3PO_4 , and H_2O are dispensed via lines **20-22** into the processing volume **12** of the process chamber **10**. As the H_2SO_4 , H_3PO_4 , and H_2O are supplied to the processing volume **12** of the process chamber **10**, the H_2SO_4 , H_3PO_4 , and H_2O mix to form a mixture (i.e. an etchant solution). The adjustable valves **23-25** control the flow rates of the H_2SO_4 , H_3PO_4 , and H_2O through dispense lines **20-22** so that the mixture is created so as to have a predetermined/desired concentration ratio of H_2SO_4 : H_3PO_4 : H_2O . In one embodiment, the mixture preferably has a concentration ratio of 2 parts H_2SO_4 (96% by weight), 2 parts H_3PO_4 (85% by weight), and 1 part H_2O . However, if desired, any concentration ratio can be used. Moreover, if desired, in some embodiments of the invention, only a single chemical can be used as the etchant, such as an H_3PO_4 only etchant.

[0045] The H_2SO_4 , H_3PO_4 , and H_2O continues to be supplied via lines **20-22** into the processing volume **12** until the mixture overflows the processing volume **12** into recirculation weir **11** and into recirculation line **40**. Once a predetermined volume of the etchant mixture is supplied to and formed in the closed-loop circulation system (i.e, the process chamber **10** and the recirculation line **40**), the valves **23-25** are closed, thereby discontinuing the supply of H_2SO_4 , H_3PO_4 , and H_2O to the process chamber **10**.

[0046] At this point, the pump **60** is activated, causing a cyclical flow of the mixture from the process chamber **10** (via weir **11**), through the recirculation line **40**, and back into the process chamber **10** (via the inlet manifolds **13**). As the mixture passes through the recirculation line

40, it passes through the heater **70** and the filter **80**. The heater **60** preferably heats the mixture to a temperature within a range of about 160 to 180°C, and most preferably to a temperature of about 165 °C. The mixture also passes by concentration sensor **50** and particle counter **55**, which are both operably coupled to the recirculation line **40**.

[0047] The concentration sensor **50** continuously measures the concentration ratio of the mixture (i.e. the ratio of $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4\text{:H}_2\text{O}$) as the mixture passes by in the recirculation line **40**. The continuous measurements of concentration levels can be performed many times per seconds so as to be essentially continuous or periodically according to a predetermined pattern. The concentration sensor **50** creates data signals indicative of the measured concentration ratio of the mixture and continuously transmits these signals to the process controller **200** for processing via its electrical connection. Similarly, the particle counter **55** also continuously measures the particle levels in the mixture as the mixture passes by in the recirculation line **40**. The particle counter **55** creates data signals indicative of the measured particle count/level in the mixture and continuously transmits these signals to the process controller **200** for processing via its electrical connection.

[0048] Upon receipt of each data signal from the concentration sensor **50** and particle counter **55**, the process controller **200** analyzes the data signals and compares the measured values to predetermined/desired values stored in its memory. More specifically, the measured concentration ratio is compared to a stored predetermined/desired concentration ratio to determine whether the measured concentration ratio is within a predetermined/acceptable range of the predetermined concentration ratio. The measured particle count is compared to a stored predetermined/desired particle count to determine whether the measured particle count is greater than the predetermined particle count. The predetermined concentration ratio is preferably within a range of 85% to 50% by weight phosphoric acid, 0% to 30% by weight sulfuric acid, and 15% to 20% by weight water. The predetermined/acceptable range of the concentration ratio is preferably +/- 5% by weight. The predetermined particle count is preferably within a range of 10 to 1000 counts per milliliter (ml), and most preferably about 100 counts/ml at 0.2 μm .

[0049] Upon comparing the measured concentration ratio of the mixture flowing through the recirculation line **40** to the predetermined/desired concentration ratio, the process controller **200** determines whether the measured concentration ratio is within the predetermined range

of the predetermined concentration ratio. Similarly, the process controller **200** also determines if the measured particle count of the mixture is greater than the predetermined particle count.

[0050] If the process controller **200** determines (1) that the measured concentration ratio is within the predetermined range of the predetermined concentration ratio and (2) that the measured particle count is equal to or below the predetermined particle count, no action is taken and the wafers **14** are ready for processing. However, if either (1) the measured concentration ratio is not within the predetermined range of the predetermined concentration ratio or (2) the measured particle count is not equal to or below the predetermined particle count, the process controller will take the appropriate feed and bleed actions to achieve acceptable an acceptable concentration ratio and an acceptable particle count in the mixture. The feed and bleed actions will be discussed in detail below.

[0051] Assuming that (1) that the measured concentration ratio is within the predetermined range of the predetermined concentration ratio and (2) that the measured particle count is equal to or below the predetermined particle count, the process controller sends a signal to a user interface indicating that the bath is ready for wafer etching/processing. At this time, the batch of wafers **14** are lowered into the processing volume **12** of the process chamber **10** until they are fully submerged in the mixture. The pump **60** continues to force flow of the mixture through the closed-loop circulation system during the entire loading and processing times. Both the concentration sensor **50** and the particle counter **55** continue to perform their respective measuring functions during wafer processing and loading.

[0052] As the wafers **14** are subjected to the mixture (i.e., the etchant), the silicon nitride is etched with a selectivity with respect to the silicon oxide. The silicon nitride process under normal conditions (165 °C) has a nitride etch rate of $55^{\pm 5}$ Å/min. Typical selectivity of a freshly prepared tank is approximately 40:1. This selectivity is not great enough for the shallow trench isolation (STI) processes of today. Most organizations want to limit the oxide loss to a few angstroms. As the mixture is used, phosphosilicates build up in the mixture and put a back reaction on the oxide etching, in effect, decreasing the oxide etch rate and raising the selectivity. This continues until the phosphosilicates reach saturation. At this time oxide deposition can occur, where the saturation effects can put a layer of phos-doped oxide on the wafer **14**. Thus there is a "window" of processing opportunity between saturation and

"sufficiently loaded" bath to process wafers with selectivity greater than 80:1, and possibly greater than 100:1. However, issues exist because the mixture needs to be "seasoned" with nitride dummies causing productivity loss and the bath life of the mixture to saturation is short again, causing lost productivity.

[0053] The etching system **100** is designed to regain the lost productivity by managing/controlling the level of silicates in the bath and keeping the silicates at a stable level. The etching system **100** does this by (1) closely monitoring the concentration ratio and/or the particle level of the mixture with the concentration sensor **50** and the particle counter **55** and/or (2) tightly controlling the concentration ratio and/or the particle level of the mixture concentration ratio with the automatic feed and bleed. In a typical feed and bleed process, a volume of fresh mixture (or components thereof) are added to the bath while an equal volume of "old" mixture is removed. As a result, the saturation of the phosphosilicates stays nearly constant. In addition to reduce the need to "condition" the bath of the mixture, a known volume of saturated solution needs to be kept to be added to the fresh solution so that even the initial selectivity is relatively high.

[0054] An example of the feed and bleed control concept according to an embodiment of the present invention will now be discussed. As the wafers **14** are subjected to the mixture and the silicon nitride and silicon oxide layers are selectively etched, etching by-products, including particles, build up in the mixture and the concentration ratio of the mixture will change. During this processing time, the concentration sensor **50** and the particle counter **55** continuously perform their respective measuring functions and the process controller **200** performs its data analysis functions as described above. The mixture continues to flow through the closed-loop circulation system and process the wafers **14** without any change until the process controller **200** determines that (1) the measured concentration ratio is not within the predetermined range of the predetermined concentration ratio or (2) the measured particle count is not equal to or below the predetermined particle count.

[0055] Turning first to particle level control, assume that the process controller **200** is monitoring the measured particle count and detects that the measured particle count is greater than the predetermined particle count. At this point, the process controller **200** simultaneously sends appropriate control signals to valves **33-35** and bleed valve **91**. Upon receiving the control signals, the valves **33-35** and the bleed valve **91** are switched to an open

position. Opening the bleed valve **91** bleeds (i.e. drains) the old/contaminated mixture from the closed-loop circulation system via the bleed line **90**. Opening the valves **33-35** feeds (i.e. adds) fresh H_2SO_4 , H_3PO_4 , and H_2O , in the desired ratio, to the closed-loop circulation system via the feed/spike lines **30-32**. The process controller **200** opens the valves **33-35** and the bleed valve **91** so that the feed and bleed flow rates are precisely controlled on each line **90**, **30-32**.

[0056] The bleed valve **91** is maintained in the open position until a desired volume of the old mixture is removed from the closed-loop circulation system. The valves **33-35** are also maintained in the open position until a volume of the mixture (or its components) is added to the closed-loop circulation system. The volume of the old mixture bled from the closed-loop circulation system via bleed line **90** is substantially equal to the volume of the mixture (or its components) added to the closed-loop circulation system via feed lines **30-32**. The feeding and bleeding is continued, while the wafers **14** continue to be processed, until a desired volume of the mixture has been bled and replaced that will return the particle count/level of the mixture within the closed-loop circulation system below the predetermined particle count. The user will program the appropriate volume to be bled and fed for various conditions based on measured particle level and the overall predetermined volume of mixture initially supplied to the process chamber **10**. In this way, the particle levels (which are indicative of silicate levels) within the mixture can be dynamically controlled during wafer processing.

[0057] Turning now to concentration control, assume that the process controller **200** is monitoring the measured concentration ratio of the mixture flowing through the recirculation line **40** and determines that the measured concentration ratio is not within the predetermined range of the predetermined concentration ratio. At this point, the process controller **200** simultaneously sends appropriate control signals to valves **33, 34, and/or 35** and bleed valve **91**. Upon receiving the control signals, the appropriate valve **33, 34 and/or 35** and the bleed valve **91** are switched to an open position. Opening the bleed valve **91** bleeds (i.e. drains) the old mixture from the closed-loop circulation system via the bleed line **90**. Depending on the component(s) of the mixture that is at a decreased ratio, either H_2SO_4 , H_3PO_4 , and/or H_2O is fed (i.e. added) to the mixture in the closed-loop circulation system via the feed/spike lines **30, 31, and/or 32** by activating the appropriate valve **33, 34, and/or 35**. The process

controller **200** opens the appropriate valve(s) **33, 34 and/or 35** and the bleed valve **91** so that the feed and bleed flow rates are precisely controlled on each line **90, 30-32**.

[0058] The appropriate valve(s) **33, 34, and/or 35** is maintained in the open position until a volume of H_2SO_4 , H_3PO_4 , and/or H_2O that is necessary to return the concentration ratio of the mixture remaining within the closed-loop circulation system to within the predetermined range from the predetermined concentration ratio. The bleed valve **91** is maintained in the open position until a volume of the old mixture, that is substantially equal to the volume of H_2SO_4 , H_3PO_4 , and/or H_2O added, is removed from the closed-loop circulation system. The feeding and bleeding is continued, while the wafers **14** continue to be processed. The user will program the appropriate volume to be bled and fed for various conditions based on the deviation of the measured concentration ratio from the predetermined range and the overall predetermined volume of mixture initially supplied to the process chamber **10**. In this way, the concentration ratio within the mixture can be dynamically controlled during wafer processing.

[0059] FIG. 6 is a high level flowchart showing the programming functions carried out by the process controller **200** of the etching system **200** in carrying out the present invention. FIG. 7 is an example of how the process controller **200** monitors and compares the measured particle count to predetermined particle counts, ranges, and acceptable tolerances.

[0060] Depending on processing needs, the feed and bleed controls discussed above for particle levels and the concentration ratio can be implemented separately or combined in an etching system. Moreover, the feed and bleed control of particle levels can be implemented into etching systems and methods using a single chemical etchant, such as H_3PO_4 only. The invention has developed the software and hardware control scheme necessary to maintain the phosphosilicate saturation level as well as the water concentration, which, along with the temperature, is the prime factor of the nitride, etch rate.

[0061] In summary, the present invention overcomes many of the problems of prior art etching systems and methods by implementing the aforementioned control scheme. Allowing the bath of the mixture to be partially drained and supplied with fresh mixture so the silicates concentration in the bath remains constant, the resulting etch rate of oxide will be also constant. As mentioned, the concentration of silicates can be monitored by a liquid-borne particle counter. If the particles counts increase above the desired threshold, the system will

allow the bath of the mixture to be partially drained and supplied with fresh mixture. The user will have to input the frequency and duration based on system loading and the resulting contamination counts as detected by the particle sensor (PS). The resulting nitride etch rate remains steady while the oxide etch rate decreases. Once the oxide etch rate reaches the lower allowable etch rate level (or particle counts), the bath of the mixture will be partially drained and filled back with a known volume of fresh acid bringing the particle counts (and hence the oxide etch rate to its acceptable level). This process will continue theoretically infinitely and the user decides to start a new cycle.

Example

[0062] An experiment was performed to test the effectiveness of two embodiments of the present invention. In carrying out the experiment, an acid bath was used to etch silicon nitride wafers. The bath was filtered, heated and filtered. Process sequence was chemical etching step, followed by rinse with de-ionized water, and then dry. The chemical step consisted of: Sulfuric acid 96%:Phosphoric acid (85% wt):water or phosphoric acid (85% wt): water. The chemical step consisted of either a mix of Sulfuric acid (96% wt), Phosphoric acid (85% wt) and water or a mix of phosphoric acid (85% wt) and 15% wt water. The following parameters and conditions were present and/or set:

- Concentration control to maintain the mix ratio throughout the bath
- Feed and bleed algorithm was activated
- 200 mm wafers with thermal nitride and oxide films.
- System configured with recirculation and filtration
- Bath temperature = 165 deg. C
- Prior to testing, wafers were run through dilute HF or SC1 cleaning for surface normalization.

[0063] Etch rate measurement were performed using Rudolph S300 with 49 point measurements in 5mm edge exclusion. Nitride loading effects were tested by processing full lots of nitride wafers for an extended period of time.

[0064] The following methods of control were used:

- Feed and bleed: to reduce the effect of the etch by-products. A known volume of the bath will be drained and a supply of a known chemicals volume will be

activated. The user will program the frequency and volumes of chemicals and/or water injected.

- Liquid-borne particle counting instruments: to monitor the liquid borne particles resulting from the etch process.
- Concentration sensor e.g. NIR, FT-NIR: the system will monitor the concentration of sulfuric acid, phosphoric acid and water. The user will select the setpoint and the system will maintain the setpoint by injecting the right constituent to adjust. For example, the system will inject sulfuric acid if it goes lower than the specified value.
- Regulated acid(s) supply (phosphoric and/or sulfuric acids)
- Regulated de-ionized water supply
- Chemical concentration sensor(s)
- Liquid borne particle counter
- Control algorithm

[0065] Wafers were processed following the above-described scheme using two different etchants. In one experiment, the wafers were processed using the feed and bleed algorithm for a phosphoric acid only etchant. In another experiment, the wafers were processed using the feed and bleed algorithm for a phosphoric acid-sulfuric acid mixture etchant.

Phosphoric Acid Only Etch Example

[0066] Figure 8 is a graph illustrating stability of silicon nitride and silicon oxide etch rates using the feed and bleed algorithm for a phosphoric acid only etchant according to an embodiment of the present invention. As shown in FIG. 8, the nitride etch rate was about 50 Å/min. while the oxide etch rate was 2.47 Å, yielding a selectivity of 400:1. This is significantly higher than typically obtained in conventional fresh phosphoric baths. As shown in FIG. 8, the oxide etch rate starts to decrease with the number of wafers processed. Once the oxides reaches the lower allowable limit, the feed/bleed systems was activated to inject a known volume of phosphoric acid into the bath, thus bringing the etch rate to a near zero value. The system continues the feed/bleed and maintains the etch rate at average of ~-0.08 Å/min. (or selectivity of theoretical infinity)(negative etch rate implies hypothetical film deposition).

Phosphoric Acid-Sulfuric Acid Mixture Etch Example

[0067] Figure 9 is a graph illustrating stability of silicon nitride and silicon oxide etch rates using the feed and bleed algorithm for a phosphoric acid-sulfuric acid mixture etchant according to an embodiment of the present invention. As shown in FIG. 8 above, a known concentration of silicates (as indicated by in-line particle counting) must be maintained to achieve the desired selectivity. This requires the bath to be “seasoned” when used for the very first time (virgin bath). This issue can be overcome if a batch of dummy nitride wafers are processed in the bath to bring the silicates to the level that warrant the desired selectivity. This process obviously requires time to process these wafers i.e. lower tool utilization.

[0068] Another way to overcome this issue (seasoning) is to inject the phosphoric acid with a chemical that suppresses the oxide etch rate, hence yielding the desired selectivity. Sulfuric acid as a strong oxidant was added to the phosphoric acid and the results are shown in FIG. 9. As shown in FIG. 9, the oxide etch rate was at a minimum from the start. In addition, there is no decreasing trend of the oxide etch rate (while nitride etch remains always constant), yielding high selectivity from the start. The feed and bleed system was enabled to allow known volumes of phosphoric (and or sulfuric) to be added in order to maintain the silicates concentration (or particle counts) to steady value.

[0069] Typically, a particle-cleaning system is implemented as part of the total process step. This particle removal step is an SC1 (Standard Clean 1) that consists of processing the wafers in a mix of ammonium hydroxide, hydrogen peroxide and water and aided by megasonics. This step is very effective in removing these contaminants but if the contamination level is high enough, the particle removal efficiency will diminish.

[0070] In both examples described above, once the particle level in the bath was maintained at a minimum level, the on-wafer particle addition was also maintained to its lowest possible value. Results are shown in FIG. 10 where the average particle addition was kept a near zero value. These results are better than those shown in Fig. 4 where the average particle addition was greater than 40. In addition, there is no sudden increase in the particle counts since the particle counts were maintained steady due to the constant refreshing of the bath with phosphoric acid (or a mix of phosphoric and sulfuric acids).

[0071] The foregoing discussion discloses and describes merely exemplary embodiments of the present invention. As will be understood by those skilled in this art, the invention may be embodied in other specific forms without departing from the spirit or essential characteristics

thereof. Specifically, the invention is not limited to any specific chemical make-up for the etchant used but can be used in combination with any etchant, irrespective of chemical make-up and or concentration ratio. Additionally, the invention can further include a system having capabilities and the equipment necessary to carry out only the concentration control, only the particle count control, or a combination of both. Accordingly, the disclosure of the present invention is intended to be illustrative, but not limiting, of the scope of the invention, which is set forth in the following claims.